The Development and Herbicidal Activity of Adjuvant-Containing Water-Dispersible Granule Formulations of Fluazifop-P-butyl†

Gordon A. Bell,* Carl A. Formstone, John H. N. Hammond & Rupert H. Sohm

Zeneca Agrochemicals, Yalding Technology Centre, Yalding, Kent ME18 6HN, UK

(Received 3 June 1998; revised version received 29 July 1998; accepted 12 August 1998)

Abstract: A series of 48 water-dispersible granule (WG) formulations containing 125 g kg^{-1} of the graminicide fluazifop-P-butyl have been designed containing a range of oils, wetters, emulsifiers, dispersants and salts, by modifying a template WG (YF8122). Granules with satisfactory dispersability and crush strength were obtained, which showed herbicidal activity equal to or better than the commercial 125 g kg^{-1} EC BIW formulation when tested on five species of graminaceous weeds in greenhouse tests. Differences between different constituents were small. The results indicate that it is possible to design WGs with properties which enable them to compete with conventional EC formulations. © 1998 Society of Chemical Industry

Pestic. Sci., **54**, 401–407 (1998)

Key words: emulsion concentrate; water-dispersible granule; adjuvant; fluazifop-P-butyl

1 INTRODUCTION

Except in a few special cases, all pesticides are sold and used in formulated form. While the formulator's task is to ensure that the physical properties of the formulation meet the user's requirements in respect of handling, application and storage stability, these physical properties must be coupled with adequate biological performance.

The use of adjuvants to increase the biological performance of pesticides is well-established.[1] Many adjuvants are wetters, but the term covers any added ingredient that will modify the biological effect of the active ingredient. Adjuvants are usually added as a tank mix at the time of application, but there is a growing tendency to incorporate them into the formulation itself, as this allows a much greater control of level and type.

Emulsifiable concentrate (EC) formulations are liquids, based on organic solvents, and adjuvants can thus readily be incorporated in them. Herbicide EC formulations may contain wetters at two or three times the AI content; such formulations are often called built-in-wetter (BIW) formulations. In recent years there has been a move away from solvent-based formulations towards solid formulations, which are considered to be safer and more environmentally friendly. Among the latter, water-dispersible granule (WG) formulations are becoming increasingly popular, and the design of a satisfactory additive-containing WG is therefore of current interest.

Fluazifop-P-butyl is a selective graminicide which is used on broad-leafed crops such as sugar beet. It eradicates grassy species and is sold as both EC and WG formulations, each with an AI content of 250 g kg^{-1}. There is also a commercial EC BIW formulation which contains 125 g kg^{-1} AI and twice this content (250 g kg^{-1}) of wetter. The objective of the present work was to develop a 125 g kg^{-1} WG containing suitable additives to give a biological performance comparable to that of the EC BIW formulation.

Fluazifop-P-butyl is itself a hydrophobic oil at room temperature, and the 250 g kg^{-1} WG is thought to be

* To whom correspondence should be addressed.

† One of a collection of papers on various aspects of agrochemicals research contributed by staff and collaborators of Zeneca Agrochemicals UK and Zeneca Ag Products USA. The papers were collected and collated by Dr B. C. Baldwin and Dr D. Tapolczay.

the only example of a high-strength liquid-containing WG currently in commercial production. The incorporation of a high level of adjuvant into such a formulation was therefore a major challenge in terms of formulation design.

2 EXPERIMENTAL METHODS

2.1 Formulation methods

The formulation of a single WG requires many iterative steps. The objective in this instance was to develop a 125 g kg^{-1} WG having acceptable physical properties and biological activity comparable to that of the commercial 125 g kg^{-1} BIW EC; this required the examination of a wide array of possible adjuvant materials. The initial stage was to design a template formulation which was flexible enough to accept many different adjuvant materials. The method chosen was to design a formulation which would cope with the most difficult case, in the hope that this would be able to cope with the others.

2.1.1 Preparation of formulations
Samples were prepared by extrusion on a 50- to 100-g scale using a laboratory Hobart mixer/extruder (model NT50). This machine was used for all three steps in the granulation process. The dry ingredients were blended as powders, followed by a wet blending step where enough water (5–15% w/w) was added to allow granulation to occur during extrusion through relatively large orifice plates (5-mm holes). This allowed the optimum water content to be determined and ensured a standard amount of paste shearing. This was followed by extrusion through 1-mm holes and drying at 50°C over 20 min in a laboratory fluid bed drier (Retsch model TG1).

2.1.2 Test methods
2.1.2.1 Dispersion properties. A sample of WG (0·01 g) was placed in tap water (100 g) at 20°C in a BS658 stoppered measuring cylinder, which was agitated end over end at 30 rev min^{-1}. The dispersion time was assessed visually; measurements were repeated three times to an error of ± 10 s. The template formulation dispersed in 50 s, but samples dispersing in 150 s or less were deemed acceptable; those with longer dispersion times were rejected.

The quality of the dispersion formed was assessed by placing 50 g WG in 300 g of tap water for 10 min in a 600-ml Pyrex square-formed beaker. The samples were then poured slowly through a 100-mesh BS sieve and the quantity retained in the vessel was dried and weighed. Samples with residues above 2% w/w were rejected. The amount remaining on the sieve was also dried and weighed; the specification for the amount retained was set at 0·01% w/w maximum.

2.1.2.2 Hardness. The hardness of all formulations was assessed subjectively by crushing a small sample (*c.* 0·01 g) under the tip of a spatula, and comparing with a sample of the commercial 250 g kg^{-1} fluazifop-P-butyl WG. This was carried out three times.

The hardness of selected samples was measured using a Stevens QTS 25 (Stevens Advanced Weighing Systems Ltd, DP House, Greenbank Technology Park, Challenge Way, Blackburn, Lancs BB1 5QB) uniaxial crush tester. For each measurement a single granule was placed on a metal platform, and a second movable plate was used to close the gap between the two, thereby crushing the sample. This was carried out at a controlled rate (2 mm s^{-1}). A pressure sensor allowed the measurement of a force-against-distance plot. Hardness was recorded as the average peak force from ten measurements.

2.2 Herbicidal activity

Each WG formulation was tested on five plant species, *Avena fatua* L. (wild oat) *Digitaria sanguinalis* (L.) Scop. (large crabgrass), *Lolium multiflorum* Lam. (Italian ryegrass), *Setaria viridis* (L.) Beauv. (green foxtail) and *Triticum aestivum* L. (wheat). The growth stages sought were three- to four-leaf stage for all species. Across tests, actual growth stages ranged from four leaves to one or two tillers (*A. fatua*), three to six leaves to one to four tillers (*D. sanguinalis*), four to five leaves to two to three tillers (*L. multiflorum*), four to six leaves to two to three tillers (*S. viridis*) and three to four leaves and zero to two tillers (*T. aestivum*).

Plants were sprayed using a track sprayer at 200 litre ha^{-1} spray volume at application rates from 30 to 110 g AI ha^{-1}, with four applied rates for each test series. After application test plants were grown in a glasshouse set at 16°C day, 12°C night with a 14-h photoperiod.

Visual damage assessments (% damage, where 0 = unaffected and 100% = complete kill.; mean of three replicates) were carried out 21–22 days after treatment. In all tests 125 g kg^{-1} EC with 250 BIW, and the template WG formulation (YF8122) were included for comparison. The statistics programme PC SAS (SAS Institute Inc., SAS Campus Drive, Cary, NC 27513, USA) was used to calculate both ED_{90} values, and potencies relative to the WG formulation (YF8122).

3 RESULTS AND DISCUSSION

3.1 Formulation

The objective was to develop a fluazifop-P-butyl 125 g kg^{-1} WG with satisfactory hardness and disper-

sion properties (i.e. meeting the specifications given in Section 2) and having biological performance comparable to the 125 g kg^{-1} EC BIW formulation. The formulation ingredients examined for their effect on performance were: oil, wetter, emulsifier, dispersant and salt. Each of these ingredients had to be assessed in a dual role, firstly as an ingredient affecting the physical properties of the formulation and secondly as an adjuvant influencing its biological performance.

A water-dispersible granule must have a solid particulate network to provide dry strength. This network has to be held together by a water-soluble component, and typically this will be a dispersant such as the naphthalene sulphonate formaldehyde condensate, 'Morwet D425'. A base formulation consisting of 5 g Morwet D425 and 95 g talc (magnesium silicate) as filler was thus prepared.

The effects of liquid components on the hardness of this simple starting formulation are shown in Fig. 1. The oils were selected (Table 1) to cover a range of polarities from glycerol, which is water-miscible, to 'Atplus' 463, a commercial emulsifiable non-polar oil. These were added to the formulation at 50 g kg^{-1}. In the case where the added oil was the AI the quantity was also 50 g kg^{-1}.

With the exception of methyl oleate, hardness was found to be inversely related to the polarity of the oil. It is thought that the weakening effect is related to solubilisation or softening of the dispersant which holds the particles together. Methyl oleate is well known as a plasticiser and the discrepancy in the series may reflect this property, rather than solubilisation.

The effect of oil quantity on granule hardness for three combinations of dispersant and oil is shown in Fig. 2. Hardness falls quite rapidly with increased oil content. The influence of oil polarity is also confirmed, glycerol reducing hardness more than 'Atplus' 463. The dispersant Polyfon H was less prone to cause softening than was Morwet D425. Thus, in order to design a WG

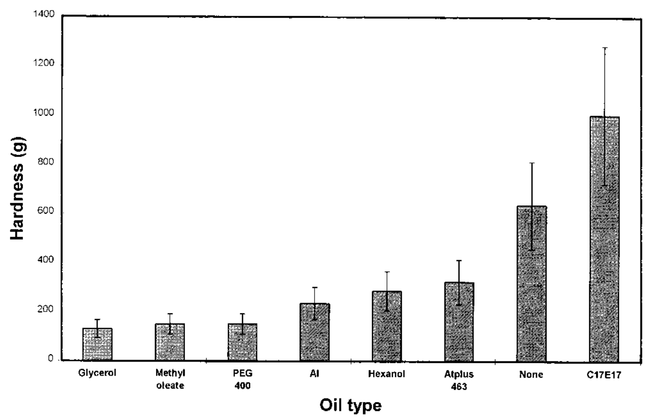

Fig. 1. WG hardness for a range of oil or wax materials added at 5%. The AI (fluazifop-P-butyl) was also added at 5%. C17E17 is a 17-carbon alkane ethoxylate surfactant with 17 moles of ethylene oxide. Bars show standard deviations.

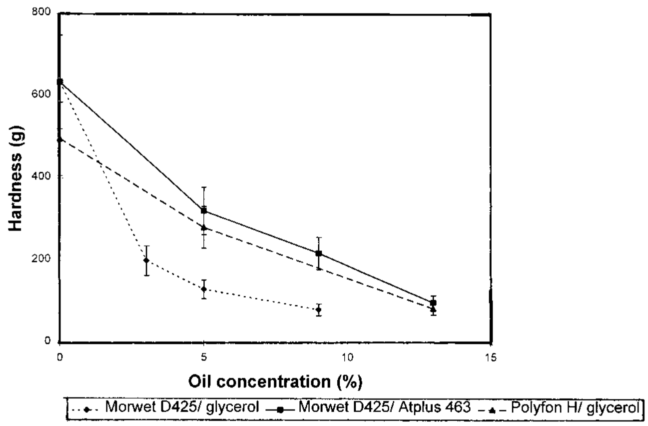

Fig. 2. WG hardness versus oil content for three combinations of dispersant and oil. Bars show standard deviations.

containing an oil adjuvant it would be sensible to use low-polarity oils, and to select the dispersant carefully. The wetting agents which are commonly used as adjuvants are also good solubilisers and hence may adversely affect hardness, so a balance must be made by dilution with a non-polar oil such as soya bean oil. Combinations of oil and liquid non-ionic surfactants are very common as tank-mix adjuvants, and such mixtures are to be preferred in WG formulations to the surfactant alone. The latter forms liquid crystals on addition to water, with a consequent rise in viscosity; where this occurs in WG formulations, the dispersion time is significantly increased.[2] However it has been reported that the oil component has considerably less influence on the biological efficacy than the non-ionic surfactant.[3] The balance between biological efficacy, WG strength and dilution behaviour is therefore important.

High-ethylene-oxide-content non-ionic surfactants can also be used as adjuvants; they are waxy in character, and, unlike liquid adjuvants, they can add to the strength of a WG, as has been demonstrated with C17E17 in Fig. 1. They are not normally used in WG formulations because they increase dispersion time, as shown in Fig. 3. This arises from their tendency to form highly viscous hexagonal or cubic phase liquid crystals.[4] As in the case of liquid non-ionic surfactants, oil can be used to reduce this problem, depending on the oil-solubility of the wax.

The use of low-polarity oil in a WG formulation necessitates the use of an emulsifier so that the oil can be evenly dispersed in the spray tank. The non-ionic surfactant wetters used as adjuvants do have some emulsifying properties, but these are rarely good enough on their own. The efficient emulsifiers are often polymers or high-ethylene-oxide-chain-length non-ionics, which can be slow to dissolve in water. They are used, however, in relatively small amounts, and so this may not be a serious drawback.

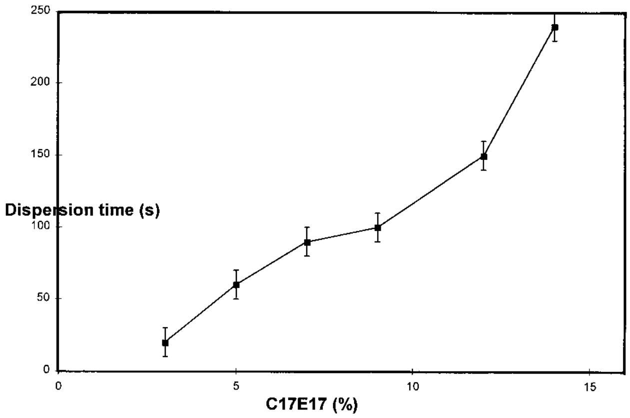

Fig. 3. WG dispersion time versus C17E17 content. Bars show standard deviations.

A blend of non-polar oil, emulsifier, adjuvant wetter, dispersant/binder, solid substrate particles and active ingredient has therefore to be formulated carefully to provide reasonable granule strength and aqueous dispersion and emulsification properties. The problem of balancing the physical properties becomes worse as the loading of liquid is increased. At high loadings the void spaces between the particles are filled and it becomes difficult for the granules to break up in water. The use of water-soluble particles, such as a salt, helps to overcome this problem, but because salts are soft they may reduce the strength of the WG. In addition they show poor absorptivity of oils. A balance is therefore required between the soluble and insoluble fillers used.

By balancing these effects the template formulation YF8122 (Table 1) was designed.

The array of ingredients to be tested by substitution in the template WG formulation was 15 oils, 20 wetters, four emulsifiers, five dispersants and four salts. These numbers are not excessive in relation to those available, and in each category it would have been possible to select very many more. Nevertheless the full range of options based on this small matrix would have been 24 000. This was considered too many and an array where one component at a time was changed from the standard (YF8122) allowed a smaller number to be selected (48) for biological testing. These formulations vary from each other in that one component has been switched for another of the same category. In order to analyse this large database of results comparisons were made between variations in each category of additive.

TABLE 1
The Template WG Formulation YF8122

Ingredient	*g kg^{-1}*	*Category*
Fluazifop-P-butyl	125	AI
Soya bean oil	75	Oil
Atlox 4848	60	Wetter
Synperonic NP13	40	Emulsifier
Morwet D425	150	Dispersant
Sodium acetate	100	Salt
Magnesium silicate	450	Filler

3.2 Biology

Table 2 shows the relative potency values for the template WG formulation compared to the standard EC formulation in three sets of greenhouse tests. Where the results were found to be statistically different the WG was superior to the EC. As some of the results indicated equivalent performance between the two formulations it has been concluded that the WG matched the efficacy of the EC.

Figure 4 (A–E) shows the rate responses that were measured for *S. viridis*. The graphs have been selected to show the best and worst performance in each test for the oils, wetters, emulsifiers, dispersants and salts, compared to the template WG and the standard EC.

The most effective oil of the 15 tested was crude rapeseed, with a high erucic acid content. This oil gave a better performance on all five species compared to the WG template. The poorest weed control was obtained with castor oil (first pressings). The oil used in the template formulation, soya bean, was one of the poorer performers. Six of the other oils were similar in performance to soya bean oil, whereas the rest were better on at least two species of plant. The EC standard proved to be less active than the WG template formulation on four of the five species. The percentage weed control results for the best and worst oils, across the five weed species (50 g ha^{-1} application rate) are shown in Table 3. The template WG and the EC results are also shown.

None of the WG variants containing alternative wetters proved to be superior to the standard WG across all of the weed species. This was surprising in view of the large number tested ($n = 20$). Eleven of the wetters were found to be not different statistically, and the rest were inferior on at least two species. The low concentration of wetter may have been a factor which made discrimination between the formulations difficult. Soprophor 3D33 performed best and Synperonic NP8, the wetter in the EC standard, was found to be one of

TABLE 2
Potency Values for the Template WG (YF8122) Formulation relative to the Standard EC in Three Greenhouse Tests

Test	Avena fatua	Digitaria sanguinalis	Lolium multiflorum	Setaria viridis	Triticum aestivum
1	0·84	0·83	**1·33**	0·92	1·01
2	**1·92**	**1·56**		**1·52**	
3	**1·59**		1·10	**1·59**	**1·56**

The potencies which display statistically significant differences ($P > 1{\cdot}2$) between the two formulations are shown in bold.

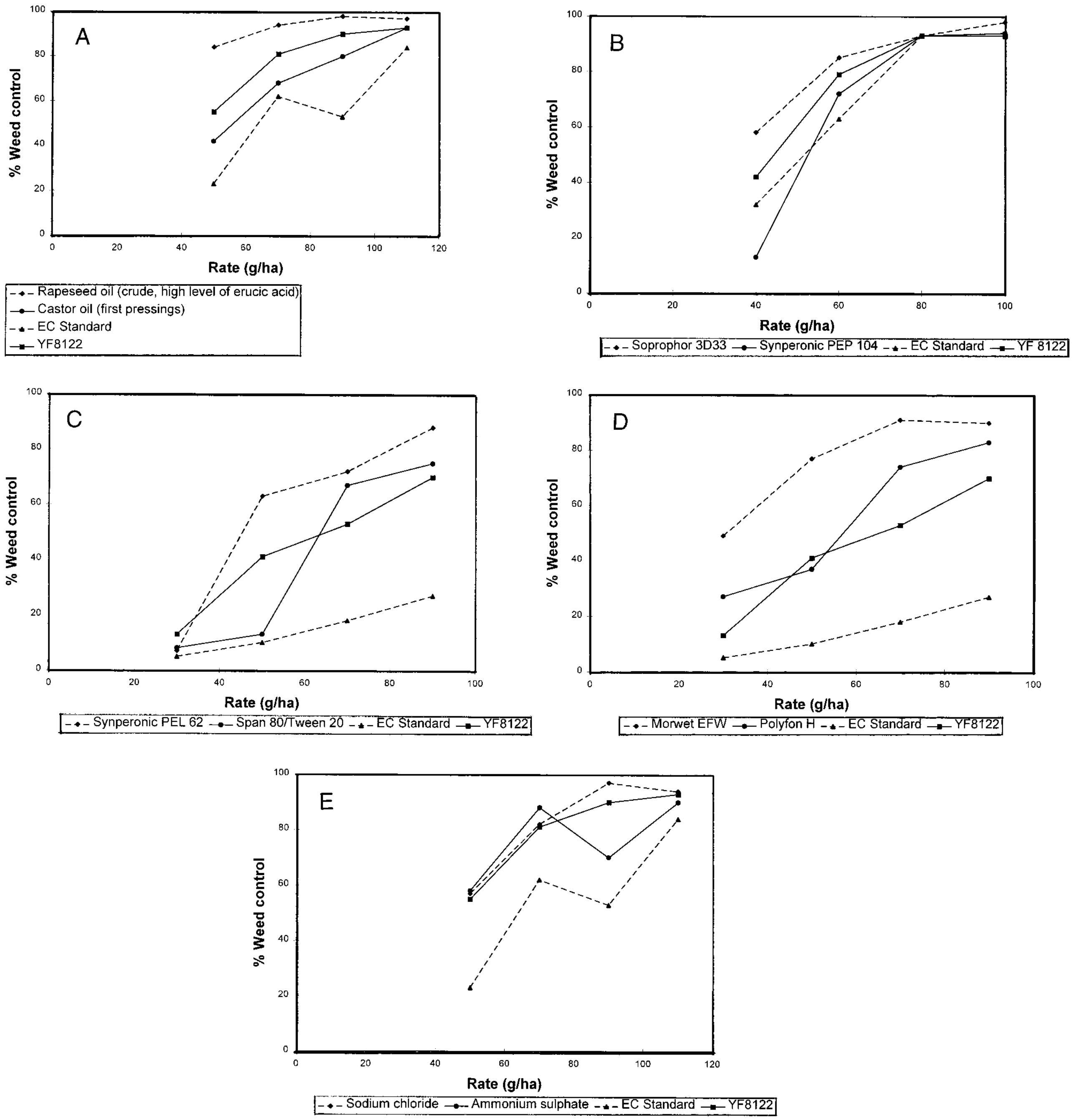

Fig. 4. Control of *Setaria viridis* by increasing amounts of components, compared to the template WG (YF8122) and standard EC formulation. The components changing in concentration are A. oil; B. wetter; C. emulsifier; D. dispersant and E. salt.

the poorer performers in the WG. The design of the commercial EC included optimisation of both the type of wetter and the concentration. Many of the wetters tested in this study, however, could not be formulated into an EC formulation, so they were not screened at that time. An explanation of the poor performance of Synperonic NP8 in the WG is therefore not available. It may have been a concentration effect, or it may indicate that the mode of action of the wetter was different in the EC compared to the WG. The percentage weed control results for the best and worst wetters, across the five weed species (40 g ha^{-1} application rate) are shown in Table 4. The template WG and the EC results are also shown.

Alternative emulsifiers which gave acceptable formulation properties were difficult to find. A small range was tested ($n = 4$), only one of which proved to be biologically superior to the template WG. All of the WG formulations were superior to the EC standard.

All of the alternative dispersants ($n = 5$) showed some advantage over the template, being either superior or equal on each weed species. This was not expected because the dispersants selected have not previously been reported as adjuvants. Lipophilic compounds

TABLE 3
Control of Five Species of Weed at an Fluazifop-P-butyl Rate of 50 g ha^{-1}

	Control (%)				
	A. fatua	D. sanguinalis	L. multiflorum	S. viridis	T. aestivum
Rapeseed oil (crude, high level of erucic acid)	89	96	74	84	78
Castor oil (first pressings)	94	83	53	42	68
WG template	57	82	47	55	64
EC standard	15	42	37	23	17

Samples include WG formulations containing the best and worst oil adjuvants, the template WG formulation and the EC standard.

usually respond to lipophilic adjuvants and not to highly water-soluble ones, such as these dispersants. The most effective dispersant, 'Morwet EFW', is also a good wetting agent and this may have been important. However the order of performance of the other dispersants could not be explained in this way.

The number of salt variants was small ($n = 4$), and they were found to be statistically similar.

Surfactants are known to enhance the efficacy of pesticides by altering the conditions of leaf retention.[5] This can be of particular importance on glasshouse-grown plants. The EC formulation contains a high level of wetters selected to improve the retention of the AI on the leaf surface. The WG formulations contain a much lower content of such wetters, but they match the EC in biological performance, suggesting that retention is not a major factor in their performance.

As mentioned earlier the number of possible variants based on the WG template was very large. The method used to select samples meant that those tested varied from one another in relatively small ways. Several of these small variations led to improvements in performance.

It is often assumed that liquid formulations of herbicides are more active than solid formulations. This work has shown that, by careful selection of ingredients, it is possible to produce a WG formulation with satisfactory physical properties which equals or exceeds the biological performance of the best EC formulation. However the work involved is time-consuming, and, even then, only a small fraction of the possible adjuvant combinations can be tested. A detailed study of the mode of action of adjuvants in WG formulations (which may be different from those in liquids) would be valuable in that it would give a rational basis for the selection of ingredients and reduce the need to rely on testing a matrix of combinations.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the work of Dr D. J. Collins and his team in the Weed Science Department at Jealott's Hill Research Station.

REFERENCES

1. Foy, C. L., Adjuvants—Current trends and technology. In *Pesticide Formulation and Adjuvant Technology*, ed. C. L.

TABLE 4
Control of Five Species of Weed at a Fluazifop-P-butyl Rate of 60 g ha^{-1}

	Control (%)				
	A. fatua	D. sanguinalis	L. multiflorum	S. viridis	T. aestivum
Soprophor 3D33	82	93	55	85	63
Synperonic NP8	59	75	58	72	32
WG standard	90	87	57	79	37
EC standard	62	85	86	63	40

Samples include WG formulations containing the best and worst wetter adjuvants, the template WG formulation and the EC standard.

Foy & D. W. Pritchard. CRC Press Inc., Boca Raton, USA, 1996, pp. 323–49.
2. Bell, G. A., Granule dispersion mechanisms. In *Formulation—from design to delivery*. Royal Society of Chemistry, London, 1997.
3. DeRuiter, H., Uffing, A. J. M. & Meinen, E., Influence of emulsifiable oils and emulsifier on the performance of phenmedipham, metoxuron, sethoxydim and quizalofop. *Meded, Fac. Landbouww. Univ. Gent*, **62** (1997) 189–98.
4. Clint, J. H., *Surfactant Aggregation*. Blackie, Glasgow, 1992, p. 166.
5. Wirth, W., Mechanisms controlling leaf retention of agricultural spray solutions. *Pestic. Sci.*, **33** (1991) 411–20.